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**(54) [Title of the Invention]**

**Polyester Resin Composition Used For Calendering,  
and a Sheet Using the Same**

**(57) [Summary]**

**[Object]** To provide a polyester resin composition that enables sheet calendering with excellent quality, in which resin sheets can be released easily from the rolls during calendering, and the finished sheet has good transparency.

**[Means of Achievement]** A polyester resin composition used for calendering, comprising a mixture in which 0.01 to 5 weight parts of a lubricant are added to a non-crystalline polyester, and characterized in that the softening point of the mixture is less than 200°C.

**[Claims]**

**[Claim 1]** A polyester resin composition used for calendering, comprising a mixture in which 0.01 to 5 weight parts of a lubricant are added to a non-crystalline polyester, and characterized in that the softening point of the mixture is less than 200°C.

**[Claim 2]** The polyester resin composition used for calendering according to claim 1, characterized in that the non-crystalline polyester comprises 30 mol% or more of terephthalic acid with respect to the total quantity of carboxylic acid components, and 30 mol% or more of ethylene glycol with respect to the total quantity of diol components, and also comprises 5 to 70 mol% of isophthalic acid with respect to the total quantity of dicarboxylic acid components and/or 5 to 70 mol% of at least one type of diol component selected from the group comprising 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, diethylene glycol, and cyclohexanedimethanol with respect to the total quantity of diol components.

**[Claim 3]** A sheet molded by means of calendering the polyester resin composition according to claim 1 or 2.

**[Detailed Description of the Invention]**

**[0001]**

**[Technological Field of the Invention]** The present invention relates to a polyester resin composition that is optimal for calendering; that has excellent release properties from a roll during calendering, long-run workability, thermal stability, and particularly, transparency in a calendered sheet; and that is useful in shrink labeling used for food products, cosmetics, and beverages, as well as in aroma-retaining heat sealed film, oil-resistant multilayer sheeting, and other various sheets and films, and particularly in sheets and films used in industrial processes. The present invention also relates to a sheet molded from this polyester resin composition.

**[0002]**

**[Prior Art]** Vinyl chloride sheeting (film) has conventionally been widely used in a variety of applications because of its low cost and excellent transparency. Extrusion molding and calender molding are known as methods for working this sheeting, but friction with the die lips in extrusion molding affects the workability (moldability) of the resin more than in calender molding, which lowers the precision of the sheet (film) thickness, width, flow direction, and the like, and this method is ill-suited for large-scale production. The latter method is therefore more widely employed for the sake of productivity and quality. Because the flexibility of vinyl chloride can be freely adjusted by means of the addition of plasticizers, it is easily workable in the form of a sheet, and an example of an application thereof is in decorative sheeting (film) imprinted with wood grain for enhancing the design of wood. However, due to drawbacks whereby dioxin is released during incineration of vinyl chloride, and restrictions on the use of plasticizers due to the presence of endocrine disrupting chemicals, a changeover from vinyl chloride sheeting (film) to other materials has been under way in recent years. Among substitute materials, polyester is favored for its physical aspects, cost, and other attributes. However, using polyester as a substitute has the following significant drawbacks.

**[0003]** One drawback is the difficulty of applying polyester to calender molding, which is widely used as a molding method for polyvinyl chloride. Extrusion molding has mainly been used conventionally as a method for manufacturing sheets and films from polyester resin for its ease of fabrication. However, molding is difficult when calendering is attempted using polyester resin, because of its relatively strong adhesion to the rolls when thermoplasticized, and its tendency to adhere to the rolls during fabrication. The addition of various lubricants has therefore been attempted in order to prevent adhesion to the rolls.

**[0004]** Lubricants that have thus been investigated include, for example, polyethylene wax, paraffin wax, and other hydrocarbon lubricants; higher fatty acid lubricants, higher alcohol lubricants, metallic soaps made from higher fatty acids, fatty acid amide lubricants, ester lubricants, and various other lubricants. For example, non-crystalline polyethylene terephthalate copolymerized with cyclohexanedimethanol has been made into a sheet by means of calendering using various lubricants in JP (Kokai) No. 11-343353, 2000-136294, 2000-186191, 2000-302951, 2001-64496, 2001-4019, and US Patent No. 6068910. However, the inventors and others have investigated various admixtures according to these disclosures using this polyester,

but the transparency of the finished sheet declines if the quantity of lubricant is increased in order to improve roll release properties, and the proper balance between the quantity of polyester and lubricant has been impossible to achieve.

**[0005]**

**[Problems That the Invention Is Intended to Solve]** An object of the present invention is to overcome the drawbacks of the prior art by means of providing a polyester resin composition that has excellent roll release properties, long-run workability, and thermal stability and that is optimal for calendering.

**[Means Used to Solve the Above-Mentioned Problems]** As a result of concentrated investigation aimed at overcoming the foregoing drawbacks, the inventors discovered that the softening point of a mixture of a non-crystalline polyester resin and a lubricant is intimately correlated with the release properties of a molten sheet from a calender roll during calendering, and to the transparency of the sheet, and thus developed the present invention.

**[0006]** Specifically, the present invention comprises the following characteristics.

(1) A polyester resin composition used for calendering, comprising a mixture of a non-crystalline polyester with a lubricant, wherein the mixture is characterized in that the softening point thereof is less than 200°C.

(2) The polyester resin composition used for calendering according to (1), characterized in that the non-crystalline polyester comprises 30 mol% or more of terephthalic acid with respect to the total quantity of carboxylic acid components, and 30 mol% or more of ethylene glycol with respect to the total quantity of diol components, and also comprises 5 to 70 mol% of isophthalic acid with respect to the total quantity of dicarboxylic acid components and/or 5 to 70 mol% of at least one type of diol component selected from the group comprising 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, diethylene glycol, and cyclohexanedimethanol with respect to the total quantity of diol components.

(3) A sheet molded by means of calendering the polyester resin composition according to (1) or (2).

[0007]

**[Embodiments of the Invention]** The polyester resin composition of the present invention used for calendering consists of a mixture of a non-crystalline polyester with a lubricant, and the softening point of the mixture is less than 200°C. "Non-crystalline" as mentioned herein is defined as follows. Specifically, using a differential scanning calorimeter (DSC), the temperature of the product is raised from -100°C to 300°C at a rate of 20°C/minute, the product is cooled from 300°C to -100°C at a rate of 50°C/min, and then the temperature is raised again from -100°C to 300°C at a rate of 20°C/min. The product is non-crystalline if it does not have a distinct fusion peak during either of the two temperature increases.

[0008] The polyester resin used in the present invention preferably comprises 30 mol% or more of terephthalic acid with respect to the total quantity of carboxylic acid components therein. 35 mol% or more is more preferred, and 40 mol% or more is most preferred. Having less than 30 mol% or more of terephthalic acid is not preferred, because the mechanical solid properties of the sheet deteriorate.

[0009] The polyester resin used in the present invention preferably comprises 30 mol% or more of ethylene glycol components with respect to the total quantity of diol components. 35 mol% or more is more preferred, and 40 mol% or more is most preferred. Having less than 30 mol% or more of ethylene glycol is not preferred, because the mechanical solid properties of the sheet deteriorate.

[0010] The polyester resin used in the present invention preferably comprises 5 to 70 mol% of isophthalic acid with respect to the total quantity of dicarboxylic acid components and/or 5 to 70 mol% of at least one type of diol component selected from the group comprising 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, diethylene glycol, and cyclohexanedimethanol with respect to the total quantity of diol components. A maximum of 65 mol% is more preferred, and a maximum of 60 mol% is most preferred. A minimum of 9 mol% is more preferred, and a minimum of 12 mol% is most preferred. Suitability for calendering can be enhanced by means of introducing these copolymer components into the molecular chain in moderation to rid the product of the crystallinity of polyethylene terephthalate and appropriately adjusting its physical properties. Among these components, isophthalic acid, neopentyl glycol, diethylene glycol, and cyclohexanedimethanol are preferred for their economical aspects, and furthermore, copolymerizing 5 to 70 mol% of

neopentyl glycol is most preferred when considering its compatibility with the lubricant added in order to impart calenderability.

[0011] Polycarboxylic acid and polyhydric alcohol components other than the abovementioned terephthalic acid, isophthalic acid, ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, neopentyl glycol, diethylene glycol, and cyclohexanedimethanol may be copolymerized with the polyester resin of the present invention. Examples of polycarboxylic acids include orthophthalic acid, 1,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 4,4'-diphenyl dicarboxylic acid, 2,2'-diphenyl dicarboxylic acid, 4,4'-diphenyl ether dicarboxylic acid, and other aromatic dibasic acids; adipic acid, azelaic acid, sebacic acid, 1,4-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid, 1,2-cyclohexane dicarboxylic acid, 4-methyl-1,2-cyclohexane dicarboxylic acid, dimer acids, trimellitic acid, and other aliphatic and alicyclic acids. On the other hand, polyhydric alcohols include 1,2-butanediol, 1,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, dipropylene glycol, 2,2,4-trimethyl-1,5-pentanediol, hydroxypivalic acid neopentyl ester, ethylene oxide adducts and propylene oxide adducts of bisphenol A, ethylene oxide adducts and propylene oxide adducts of hydrogenated bisphenol A, 1,9-nonanediol, 2-methyloctanediol, 1,10-decanediol, 2-butyl-2-ethyl-1,3-propanediol, tricyclodecane dimethanol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and the like.

[0012] The number-average molecular weight of the polyester resin used in the present invention is preferably 15,000 to 40,000. A minimum of 18,000 is more preferred, and a minimum of 20,000 is even more preferred. A maximum of 38,000 is more preferred, and a maximum of 35,000 is even more preferred. If the number-average molecular weight is less than 15,000, the strength and elongation of the sheet is inadequate, due to inadequate resin cohesion, which makes it brittle and unusable. On the other hand, because the melt viscosity rises if the number-average molecular weight is 40,000 or above, the optimal temperature for calendering also rises, which results in poor roll release properties in the sheet.

[0013] The acid value of the polyester resin of the present invention used for calendering is preferably  $60 \text{ eq}/10^6 \text{ g}$  or lower, more preferably  $50 \text{ eq}/10^6 \text{ g}$  or lower, and even more preferably  $40 \text{ eq}/10^6 \text{ g}$  or lower. If the acid value is more than  $60 \text{ eq}/10^6 \text{ g}$ , hydrolysis is further accelerated when the resin is heated during calendering, and the mechanical strength of the finished sheet is

reduced. The roll release properties of the sheet also decline as decomposition of the resin progresses.

[0014] The melt viscosity of the polyester resin used in the present invention is preferably 5,000 to 60,000 dPa·sec when at 220°C and a shear speed of 100 sec<sup>-1</sup>. A more preferred minimum is 6,000 dPa·sec, and an even more preferred minimum is 7,000 dPa·sec. A more preferred maximum is 50,000 dPa·sec, and an even more preferred maximum is 40,000 dPa·sec. If the melt viscosity is less than 5,000 dPa·sec, the roll release properties of the sheet decline due to increased adhesion of the resin. On the other hand, a melt viscosity of over 60,000 dPa·sec is too high, and the resultant decrease in productivity makes it impractical.

[0015] When a sheet is made by means of calendering using the polyester resin of the present invention, a lubricant must be admixed with the polyester resin in order to improve the roll release properties of the molten sheet.

[0016] The admixed quantity of the lubricant used in the present invention is 0.01 to 5 weight parts. A preferred minimum is 0.05 weight parts, a more preferred minimum is 0.1 weight parts, and an even more preferred minimum is 0.2 weight parts. Also, a preferred maximum is 4.5 weight parts, a more preferred maximum is 4 weight parts, and an even more preferred maximum is 3.5 weight parts. If the quantity of the lubricant is less than 0.01 weight parts, enhancement to the roll release properties is difficult to obtain, and if the quantity is more than 5 weight parts, the transparency, coloration, and printability of the processed sheet show a tendency to decline.

[0017] Lubricants used in the present invention include polyolefinic waxes, metal salts of organic phosphate esters, organic phosphate esters, ester compounds of adipic acid or azelaic acid with higher aliphatic alcohols, ethylene bis-stearamides, methylene bis-stearamides, ester compounds of glycerin with higher aliphatic acids, ester compounds of pentaerythritol with higher aliphatic acids, higher aliphatic alcohols, higher aliphatic acids, paraffins derived from petroleum or coal, waxes, natural or synthetic polyester waxes, metallic soaps made from higher aliphatic acids, and the like. These may be used in combinations of one, two, or more types thereof. Using a polyolefinic wax and/or metal salt of an organic phosphate ester is particularly preferred, because the roll release properties of the sheet and the transparency of the finished sheet can be easily obtained at the same time.

[0018] Polyolefinic waxes used as lubricants in the present invention include polyethylene wax, polypropylene wax, and derivatives of these, and these derivatives include copolymers with other monomers, such as acrylic acid, vinyl acetate, styrene, and maleic acid, and partially oxidized decomposition products.

[0019] Metal salts of organic phosphate esters used as lubricants in the present invention include, for example, metal salts of the organic phosphate ester indicated by the general formula (I) below and/or metal salts of the organic phosphate ester indicated by the general formula (II) below.

Formula (I):  $[\{RO(C_fH_{2f}O)_n\}_{3-a-o}PO(O)_a(OH)_e]_d\{M(OH)_b\}_c$

(In the formula, R is a hydrocarbon group with a carbon number of 4 to 30; M is an alkali metal, alkaline earth metal, Zn, or Al; a is 1 or 2; e is 0 or 1 (0 or 1 when a is 1, and 0 when a is 2); b is 0 to 2; c is 1 or 2; d is 1 to 3; f is 2 or 3; n is 0 to 60; and a, b, c, and d have the following relation with the valence (hereinafter referred to as m) of the metal (M). When m = 1, then b = 0, d = 1, and a = c; when m = 2, then b = 0, c = 1, and a × d = 2, or b = 1, d = 1, and a = c; when m = 3, then b = 0, d = 3, a = c, b = 1, c = 1 and a × d = 2, or b = 2, d = 1, and a = c; furthermore, when m ≥ 2, mutually different phosphate ion groups may be bonded with the metal (M), and in this case, d = 2 or 3 is the total number of mutually different phosphate ion groups. Also, when d is 2 or 3, each of the structures enclosed in brackets may be mutually the same or different.)

[0020] Formula (II):  $[\{R^1O(C_fH_{2f}O)_n\}_{3-a-c}PO(O)_a(OH)_e]_d\{M(OCOR^2)_s(OH)_x\}_t$

(In the formula, R<sup>1</sup> is a hydrocarbon group with a carbon number of 4 to 30; R<sup>2</sup> is an alkyl group with a carbon number of 1 to 25; M is an alkali metal, alkaline earth metal, Zn, or Al; a is 1 or 2; e is 0 or 1 (0 or 1 when a is 1, and 0 when a is 2); d is 1 or 2; s is 1 or 2; x is 0 or 1; t is 1 or 2; f is 2 or 3; and n is 0 to 60. Also, s + x = 1 or 2; and a, d, s, and t have the following relation with the valence (hereinafter referred to as m) of the metal (M). When m = 2, then s = 1, d = 1, and a = t; when m = 3, then s = 1, t = 1, and a × d = 2, or s = 2, d = 1, and a = t; and furthermore, when m = 3, mutually different phosphate ion groups may be bonded with the metal (M), and in this case, d = 2 is the total number of various phosphate ion groups. Also, when d is 2, each of the structures enclosed in brackets may be mutually the same or different.)

[0021] An alkyl group, phenyl group, arylalkyl group, alkenyl<sup>1</sup> group, or alkylphenyl group is preferred for the hydrocarbon group with a carbon number of 4 to 30 indicated by R in the abovementioned general formula (I) and the hydrocarbon group with a carbon number of 4 to 30



indicated by  $R^1$  in the abovementioned general formula (II). Also, Li, Na, K, and the like, for example, are preferred for the alkali metal indicated by M in the general formulae (I) and (II), and Mg, Ca, Ba, and the like, for example, are preferred as alkaline earth metals.

[0022] The metal salt of the organic phosphate ester indicated by the general formula (I) and the metal salt of the organic phosphate ester indicated by the general formula (II) may be manufactured by means of the usual method, and no particular limit is placed on the manufacturing method.

[0023] Preferred examples of metal salts of the organic phosphate ester indicated by the general formula (I) include chemical compounds (1) through (13) in Table 1 below, chemical compounds (14) through (16) in Table 2 below, and the like, and preferred examples of metal salts of the organic phosphate ester indicated by the general formula (II) include chemical compounds (15) through (26) in Table 2 below. These may be used singly or together in combinations of two or more types thereof.

[0024] Also, as shown by decimal fractions included in the number of repetitions of oxyethylene or oxytrimethylene units in the polyethyl alcohol component, these compounds (compounds (1) through (26)) are pure compounds or mixtures of a number of metal salts of phosphate esters having different numbers of repeating oxyethylene units or oxytrimethylene units in the polyether alcohol component (the number of repetitions (n) in  $(C_1H_2O)_n$  in the formula).

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<sup>1</sup> Translator's note: The original has "argenyl," which appears to be a typographical error.

[0025]

[Table 1]

| Compound No. | Structural Formula  | Compound No. | Structural Formula  |
|--------------|---|--------------|---|
| (1)          | $\text{C}_{18}\text{H}_{35}(\text{OCH}_2\text{CH}_2)_{1.8}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{ONa}$   | (9)          | $\text{C}_9\text{H}_{19}(\text{OCH}_2\text{CH}_2)_{10.5}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OZnOH}$   |
| (2)          | $\text{C}_8\text{H}_{17}(\text{OCH}_2\text{CH}_2)_{20.3}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OLi}$     | (10)         | $\text{C}_{20}\text{H}_{41}(\text{OCH}_2\text{CH}_2)_{4.0}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OLiOH}$ |
| (3)          | $\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2)_{14.5}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OLi}$  |              | $\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2)_{4.5}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OLiOH}$ |
| (4)          | $\text{C}_{13}\text{H}_{27}(\text{OCH}_2\text{CH}_2)_{6.9}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OMgOH}$ | (11)         | $\text{C}_{10}\text{H}_{21}(\text{OCH}_2\text{CH}_2)_{10.5}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OMg}$  |
| (5)          | $\text{C}_{14}\text{H}_{29}(\text{OCH}_2\text{CH}_2)_{4.5}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OLiOH}$ |              | $\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2)_{4.5}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OLiOH}$ |
| (6)          | $\text{C}_{13}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{7.3}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OK}$    | (12)         | $\text{C}_{18}\text{H}_{35}(\text{OCH}_2\text{CH}_2)_{34.5}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OLi}$  |
| (7)          | $\text{C}_{13}\text{H}_{27}(\text{OCH}_2\text{CH}_2)_{3.0}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OZn}$   | (13)         | $\text{C}_{13}\text{H}_{27}(\text{OCH}_2\text{CH}_2)_{6.0}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OZnOH}$ |
| (8)          | $\text{C}_{13}\text{H}_{27}(\text{OCH}_2\text{CH}_2)_{6.0}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OZn}$   |              | $\text{C}_{13}\text{H}_{27}(\text{OCH}_2\text{CH}_2)_{6.0}-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OZnOH}$ |

[0026]

[Table 2]

| Compound No. | Structural Formula   | Compound No. | Structural Formula   |
|--------------|--|--------------|--|
| (14)         | $\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2\text{CH}_2)_{4.6}\text{O}-\text{P}(=\text{O})(\text{OH})\text{ONa}$  | (21)         | $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{6.3}\text{O}-\text{P}(=\text{O})(\text{O})_2-\text{Al}-\text{C}_7\text{H}_{15}\text{COO}$  |
| (15)         | $\left[ \left( \text{C}_9\text{H}_{19} \right)_2 \text{C} = \text{C} \left( \text{OCH}_2\text{CH}_2 \right)_{5.2} \text{O} \right]_2 \text{P}(=\text{O})(\text{O})_2\text{Ca}$ | (22)         | $\left[ \text{C}_{13}\text{H}_{27}(\text{OCH}_2\text{CH}_2)_{7.0} \text{O} \right]_2 \text{P}(=\text{O})(\text{O})_2\text{AlOH}$   |
| (16)         | $\text{C}_{24}\text{H}_{48}\text{O}-\text{P}(=\text{O})(\text{O})_2\text{Zn}$  | (23)         | $\left[ \text{C}_{18}\text{H}_{33}(\text{OCH}_2\text{CH}_2)_{8.3} \text{O} \right]_2 \text{P}(=\text{O})(\text{O})_2\text{Zn}$   |
| (17)         | $\text{C}_{14}\text{H}_{29}(\text{OCH}_2\text{CH}_2)_{7.8} \text{O}-\text{P}(=\text{O})(\text{OH})\text{O}-\text{Ba}-\text{C}_{17}\text{H}_{35}\text{COO}$                     | (24)         | $\left( \text{C}_6\text{H}_5 \right)_2 \text{C} = \text{C} \left( \text{OCH}_2\text{CH}_2 \right)_{18.5} \text{O}-\text{P}(=\text{O})(\text{OH})\text{O}-\text{Ca}-\text{C}_{17}\text{H}_{35}\text{COO}$ |
| (18)         | $\text{C}_9\text{H}_{19}(\text{OCH}_2\text{CH}_2)_{5.0} \text{O}-\text{P}(=\text{O})(\text{OH})\text{O}-\text{Mg}-\text{C}_{11}\text{H}_{23}\text{COO}$                        | (25)         | $\text{C}_{18}\text{H}_{37}(\text{OCH}_2\text{CH}_2\text{CH}_2)_{11.2} \text{O}-\text{P}(=\text{O})(\text{OH})\text{O}-\text{Ba}-\text{C}_{17}\text{H}_{35}\text{COO}$                                   |
| (19)         | $\text{C}_8\text{H}_{17}(\text{OCH}_2\text{CH}_2)_{18.5} \text{O}-\text{P}(=\text{O})(\text{OH})\text{O}-\text{Ca}-\text{C}_{17}\text{H}_{35}\text{COO}$                       | (26)         | $\left( \text{C}_{13}\text{H}_{27} \right)_2 \text{C} = \text{C} \left( \text{OCH}_2\text{CH}_2 \right)_2 \text{O}-\text{P}(=\text{O})(\text{O})_2\text{Zn}-\text{C}_{11}\text{H}_{23}\text{COO}$        |
| (20)         | $\left[ \text{C}_{13}\text{H}_{27}(\text{OCH}_2\text{CH}_2)_{7.8} \text{O} \right]_2 \text{P}(=\text{O})(\text{O})_2\text{Zn}-\text{C}_{11}\text{H}_{23}\text{COO}$            |              |  |

[0027] The polyester resin composition of the present invention used for calendering has a softening point of less than 200°C, preferably less than 195°C, more preferably less than 190°C, even more preferably less than 185°C, and most preferably less than 180°C. The minimum is not particularly limited, but is 120°C or above, more preferably 130°C or above, and most preferably 140°C or above from the perspective of calenderability and working temperature. The softening point is measured according to the JIS K2207 ring and ball method using a glycerin bath. The roll release properties become poor if the softening point is over 200°C, because the roll temperature during calendering rises, and the composition becomes heavily plasticized. Specifically, good roll release properties and transparency in the sheet cannot be obtained at the same time. Particularly when attempting to obtain a sheet having a thickness of 0.2 mm or less, in order not to place a burden on the calendering device, the melt viscosity of the resin is lowered by means of using a resin with a comparatively low molecular weight, using a large quantity of internal lubricant, raising the working temperature, and by other means, but if a resin composition whose softening point is 200°C or above is used at this time, drawbacks occur whereby a balance cannot be reached between the roll release properties, sheet transparency, and controllability of uniform film thickness, and the resin sheet tends to sag when released.

[0028] The method for setting the softening point of the polyester resin composition of the present invention to 200°C is not particularly limited, but includes (1) a method whereby the type and quantity of copolymerized monomers in the polyester are varied to adjust the softening point of the polyester, which effectively adjusts the softening point of the composition; (2) a method whereby the molecular weight of the polyester is varied to adjust the softening point of the polyester, which effectively adjusts the softening point of the composition; and (3) a method whereby the softening point of the composition is adjusted by means of admixing a component to act as a plasticizer when the softening point of the polyester is high.

[0029] The abovementioned method (1) for adjusting the softening point of the polyester resin composition of the present invention consists of copolymerizing a monomer into a homopolymer such as polyethylene terephthalate so as to lower its crystallinity. More specifically, isophthalic acid, neopentyl glycol or another component that inhibits the crystallization of polyethylene terephthalate may be copolymerized therein.

[0030] The abovementioned method (2) capable of adjusting the softening point of the polyester resin composition of the present invention consists of reducing the molecular weight of the polyester as such without changing the composition of the polyester.

[0031] The abovementioned method (3) for adjusting the softening point of the polyester resin composition of the present invention may consist of directly admixing a component to act as a plasticizer, or admixing the previously described lubricant component. Examples of plasticizers include such items as those listed below. Dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dinormal octyl phthalate, 2-ethylhexylphthalate, diisooctyl phthalate, dicapryl phthalate, dinonyl phthalate, diisononyl phthalate, didecyl phthalate, diisodecyl phthalate, diundecyl phthalate, dilauryl phthalate, ditridecyl phthalate, dibenzyl phthalate, dicyclohexyl phthalate, butyl benzyl phthalate, octyl decyl phthalate, butyl octyl phthalate, octyl benzyl phthalate, *n*-hexyl *n*-decyl phthalate, *n*-octyl *n*-decyl phthalate, and other phthalic acid ester plasticizers; tricresyl phosphate, tri-2-ethylhexyl phosphate, triphenyl phosphate, 2-ethyl hexyl phenyl phosphate, cresyl diphenyl phosphate, and other phosphoric acid ester plasticizers; di-2-ethyl hexyl adipate, diisodecyl adipate, *n*-octyl *n*-decyl adipate, *n*-heptyl *n*-nonyl adipate, diisooctyl adipate, diiso-*n*-octyl adipate, di-*n*-octyl adipate, didecyl adipate, and other adipic acid ester plasticizers; dibutyl sebacate, di-2-ethylhexyl sebacate, diisooctyl sebacate, butyl benzyl sebacate, and other sebacic acid ester plasticizers; di-2-ethylhexyl azelate, dihexyl azelate, diisooctyl azelate, and other azelaic acid ester plasticizers; triethyl citrate, acetyl triethyl citrate, tributyl citrate, acetyl tributyl citrate, acetyl tri-2-ethylhexyl citrate, and other citric acid ester plasticizers; methyl phthalyl ethyl glycolate, ethyl phthalyl ethyl glycolate, butyl phthalyl butyl glycolate, and other glycolic acid ester plasticizers; tributyl trimellitate, tri-*n*-hexyl trimellitate, tri-2-ethylhexyl trimellitate, tri-*n*-octyl trimellitate, tri-isooctyl trimellitate, tri-isodecyl trimellitate, and other trimellitic acid ester plasticizers; di-2-ethylhexyl isophthalate, di-2-ethylhexyl terephthalate, and other phthalic acid isomer ester plasticizers; methyl acetyl ricinoleate, butyl acetyl ricinoleate, and other ricinoleic acid ester plasticizers; polypropylene adipate, polypropylene sebacate, modified polyesters thereof, and other polyester plasticizers; epoxidized soybean oil, epoxybutyl stearate, epoxy(2-ethylhexyl)stearate, epoxidized flaxseed

oil, 2-ethylhexyl epoxytolate,<sup>2</sup> and other epoxy plasticizers; and the like, and these may be used singly or in combinations of two or more types thereof.

[0032] Other antioxidants may be admixed in the polyester resin composition of the present invention to prevent thermal degradation of the polyester resin (to prevent coloration of the resin due to thermal degradation) during fabrication. Phenol antioxidants, organic phosphorous acid ester compounds, and the like, for example, are suitable for use as antioxidants.

[0033] In the polyester resin composition of the present invention, other components may be arbitrarily added according to the application. These components include, for example, fillers, UV absorbers, light stabilizers, pigments, antistatic agents, antimicrobial agents, epoxy<sup>3</sup> compounds, cross-linking agents, and the like.

[0034]

[Working Examples] The following working examples will be given in order to describe the present invention in further detail, but the present invention is in no way limited by the working examples. Measured values given in the synthesis examples were found by means of the measurement methods below.

Resin composition: the product was dissolved in heavy chloroform, and assayed by means of H-NMR.

Glass transition temperature: measured using a differential scanning calorimeter by placing a 10-mg measurement sample on an aluminum pan, pressing the lid closed, and measuring at a temperature increase rate of 20°C/min.

Number-average molecular weight: found as a polystyrene equivalent value by gel permeation chromatography using hexafluoroisopropanol as a solvent.

Acid value: 1 g of the resin was dissolved in 30 mL of chloroform, and the acid value was found by titrating with a 0.1 N potassium hydroxide ethanol solution. Phenolphthalein was used as an indicator.

[0035] <Synthesis example of non-crystalline polyester (A)>

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<sup>2</sup> Translator's note: "Epoxytolate" is a tentative transliteration of a chemical name that could not be found in the reference materials available to the translator.

<sup>3</sup> Translator's note: The word "epoxy" reads "eboxy" in the original, which appears to be a typographical error. This is corrected in the translation for the sake of readability.

960 weight parts of dimethyl terephthalate, 510 weight parts of ethylene glycol, 190 weight parts of neopentyl glycol, and 0.34 weight part of tetrabutyl titanate were placed in a reactor equipped with a stirrer, thermometer, and a cooler used for distillation, and transesterification was performed for two hours at 170 to 220°C. As the temperature of the reaction system was raised from 220°C to 270°C after completion of transesterification, the pressure inside the system was gradually reduced to 500 Pa over 60 minutes. Polycondensation was then performed for 55 minutes at 130 Pa or below, and non-crystalline polyester (A) was obtained.

[0036] According to NMR analysis of non-crystalline polyester (A), the dicarboxylic acid component was composed of 100 mol% of terephthalic acid, and the diol component was composed of 65 mol% of ethylene glycol and 35 mol% of neopentyl glycol. Also, the glass transition temperature thereof was 78°C, the number-average molecular weight was 28,000, and the acid value was 30 eq/10<sup>6</sup> g.

[0037] Non-crystalline polyesters (B) through (E) were manufactured in the same manner as non-crystalline polyester (A). The composition and results of measurement thereof are shown in Table 3. (numerical values are mol% in resin)

[0038]

[Table 3]

|            |  | Non-crystalline polyester synthesis examples |       |       |       |       |
|------------|--|--|-------|-------|-------|-------|
|            |  | A  | B     | C     | D     | E     |
| Acid       | Terephthalic acid                                | 100  | 90    | 88    | 85    | 100   |
|            | Isophthalic acid                                 |  | 10    |       | 15    |       |
|            | Adipic acid                                      |  |       | 12    |       |       |
| Glycol     | Ethylene glycol                                  | 65   | 85    | 78    | 72    | 70    |
|            | Diethylene glycol                                |  | 15    |       |       |       |
|            | Neopentyl glycol                                 | 35   |       |       |       |       |
|            | Cyclohexanedimethanol                            |  |       |       |       | 30    |
|            | 2-methyl-1,3-propanediol                         |  |       | 22    |       |       |
|            | 1,3-propanediol                                  |  |       |       | 28    |       |
| Properties | Number-average molecular weight                  | 28000  | 32000 | 25000 | 33000 | 29000 |
|            | Glass transition temperature (°C)                | 78   | 62    | 55    | 58    | 78    |
|            | Melting point (°C)                               | —  | —     | —     | —     | —     |
|            | Acid value (equivalent weight/10 <sup>6</sup> g) | 30   | 25    | 16    | 38    | 25    |

[0039] The polyesters shown in Table 3 were mixed with the components shown in Tables 4 and 5, and the mixture was kneaded on two 6-inch chilled rolls adjusted to 170°C. The product was mixed while occasionally peeling off the resin adhering to the chilled rolls, and after five minutes of kneading, the roll interval was set to 0.3 mm (sheet thickness set to 0.3 mm), and the molten sheet was peeled from the roll to make a film. The release properties of the sheet were evaluated based on the release properties thereof from the roll at that time. Also, the evaluation criteria were as shown below. The results are shown in Tables 4 and 5.

[0040] Sheet release properties:

⊙: Extremely good release properties from the roll

○: Release properties sufficient for practical use

×: Strong adhesion to the roll, releasing difficult, normal sheet cannot be obtained

Transparency:

⊙: Extremely transparent

○: Transparency sufficient for practical use

×: Poor transparency

[0041] In the section for evaluation of transparency, "-" indicates that evaluation was not performed because the release properties of the sheet were poor and a normal sheet could not be obtained.

Softening point: measured by a JIS K2207 ring and ball method using a glycerin bath

Also, the lubricants and plasticizers indicated in Tables 4 and 5 refer to the compounds below.

a: tridecyl poly(oxyethylene)phosphate zinc chloride

b: styrene modified polyethylene wax

c: polypropylene adipate

Also, the numerical values for the quantities of polyesters, lubricants, and plasticizers in the tables represent weight parts.



[0042]

[Table 4]

|                           |                          | Working Examples |     |     |     |     |     |     |     |     |
|---------------------------|--------------------------|------------------|-----|-----|-----|-----|-----|-----|-----|-----|
|                           |                          | 1                | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
| Non-crystalline polyester | A                        | 100              | 100 | 100 |     |     |     |     | 100 |     |
|                           | B                        |                  |     |     | 100 |     |     |     |     |     |
|                           | C                        |                  |     |     |     | 100 |     |     |     |     |
|                           | D                        |                  |     |     |     |     |     | 100 |     |     |
|                           | E                        |                  |     |     |     |     | 100 |     |     | 100 |
| Lubricant                 | a                        | 0.3              | 0.3 | 0.5 | 0.5 | 0.2 | 0.5 | 0.3 | 0.5 | 0.3 |
|                           | b                        |                  | 0.1 | 0.2 |     |     | 0.1 |     |     |     |
| Plasticizer               | c                        |                  |     |     | 5   | 5   | 10  |     | 5   | 5   |
| Evaluation                | Softening point          | 188              | 189 | 185 | 178 | 175 | 186 | 190 | 179 | 192 |
|                           | Sheet release properties | ○                | ◎   | ◎   | ○   | ○   | ○   | ○   | ○   | ○   |
|                           | Transparency             | ◎                | ◎   | ◎   | ○   | ○   | ○   | ○   | ◎   | ○   |

[0043]

[Table 5]

|                           |                          | Comparative Examples |     |     |     |     |     |
|---------------------------|--------------------------|----------------------|-----|-----|-----|-----|-----|
|                           |                          | 1                    | 2   | 3   | 4   | 5   | 6   |
| Non-crystalline polyester | A                        | 100                  | 100 |     |     |     |     |
|                           | B                        |                      |     |     |     |     |     |
|                           | C                        |                      |     |     |     |     |     |
|                           | D                        |                      |     | 100 |     |     |     |
|                           | E                        |                      |     |     | 100 | 100 | 100 |
| Lubricant                 | a                        |                      |     |     |     | 0.2 | 1   |
|                           | b                        |                      |     |     |     |     | 0.5 |
| Plasticizer               | c                        |                      | 10  |     |     |     |     |
| Evaluation                | Softening point          | 192                  | 181 | 192 | 210 | 208 | 205 |
|                           | Sheet release properties | ×                    | ×   | ×   | ×   | ×   | ○   |
|                           | Transparency             | —                    | —   | —   | —   | —   | ×   |

[0044]

**[Effect of the Invention]** As described above, the polyester resin composition of the present invention consists of a composition in which non-crystalline polyester is combined with a lubricant, and the softening point of the mixture is less than 210°C. By using this composition, the heretofore-unsatisfactory release of the sheet from the rolls during calendering of the polyester resin composition can be improved, which enables sheet calendering in which the finished sheet has good transparency and excellent quality.

Continued from front page:

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| (51) Int. Cl. <sup>7</sup> | Class. Symbols                 | FI          | Subject Codes (Reference) |
|----------------------------|--------------------------------|-------------|---------------------------|
| B 29 L 7:00                |                                | B 29 L 7:00 |                           |
| F terms (reference):       | 4F071 AA43 AA71 AA85 AC05 AC10 |             |                           |
|                            | AC15 AE11 AG21 AH04            |             |                           |
|                            | 4F204 AA24B AA24E AB07 FA06    |             |                           |
|                            | FB02 FE21 FF01 FN11 FN15       |             |                           |
|                            | FN20                           |             |                           |
|                            | 4J002 AE032 CF031 EH096 EW046  |             |                           |
|                            | FD172 FD176 GA01               |             |                           |